Atom Transfer and Single-Adatom Contacts

L. Limot,[1] J. Kröger,[1] R. Berndt,[1] A. Garcia-Lekue,[2] and W. A. Hofer[2]

[1]*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany*
[2]*Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, United Kingdom*

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The point contact of a tunnel tip approaching towards Ag(111) and Cu(111) surfaces is investigated with a low temperature scanning tunneling microscope. A sharp jump to contact, random in nature, is observed in the conductance. After point contact, the tip-apex atom is transferred to the surface, indicating that a one-atom contact is formed during the approach. In sharp contrast, the conductance over single silver and copper adatoms exhibits a smooth and reproducible transition from tunneling to contact regime. Numerical simulations show that this is a consequence of the additional dipolar bonding between the adatom and the surface atoms.

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How do mechanical and transport properties change as matter is sized down to the atomic scale? This question is considered of fundamental interest and potentially important in view of future nanoscale device technologies. It is also of particular interest for our understanding of technologically important problems like friction, machining, lubrication, and adhesion, where the contact between macroscopic bodies occurs typically at numerous atomic-size protrusions, whose properties determine those of the macroscopic contact. Proximity probes like the scanning tunneling microscope (STM), metal break junctions, and related techniques, together with computational methods for simulating tip-sample interactions with atomic detail, have enabled to address this question by investigating atomic-size contacts [1]. Metallic point contacts between two metallic surfaces are known to exhibit a jump in the conductance [2–4]. When stretched to the point of breaking, their conductance decreases in discrete steps of $\sim 2e^2/h$ [5–7], the conductance expected for a one-dimensional conductor with one propagating channel. Since the shape of this staircase is material dependent, the chemical valance of the contact atoms is likely fixing the number of conduction channels [8]. The reverse process—a STM tip approaching a metallic surface at close range and creating a contact, as opposed to the stretching and breaking of contacts—is far less documented. This is quite surprising since the STM allows for measurements with knowledge of identity, location, and number of atoms in between electrodes. A pioneering investigation of this type was performed on a single Xe atom and a two-Xe-atom chain using a W tip and a nickel surface [9]. Xe did not exhibit metallic behavior, which is reflected by the low conductance observed for the contacts (below 0.2 in units of $2e^2/h$). In the present Letter, we report an investigation of well defined metallic contacts. Using a low temperature STM, we create single-atom contacts by lowering the tip over isolated metallic adatoms, Ag atoms on Ag(111), and Cu atoms on Cu(111). Unlike tip-surface contacts where a sharp jump in the conductance is observed, tip-adatom contacts exhibit a smooth and reproducible variation from tunneling to contact regime. A numerical analysis indicates that the additional dipolar bonding of the adatom compared to surface atoms explains this surprising finding. Moreover, we show that the jump to contact over the clean surfaces also results in the transfer of the tip-apex atom to the surface. This is experimental evidence that a one-atom contact is formed when the tip is in close proximity to a clean surface, as usually inferred from the value of $G \sim 1$ (in units of $2e^2/h$) at point contact.

The experiments were performed in a custom-built ultrahigh vacuum STM operating at 4.6 K using Ag(111) and Cu(111) surfaces—cleaned by Ar^+ sputter/anneal cycles. The W tip was first electrochemically etched *ex situ*, and then prepared *in situ* by soft indentations into the surface, until adatoms were imaged spherically [see Fig. 2(c)]. Given this preparation, the tip is covered with surface material. The conductance ($G = I/V$, where I is the tunneling current) versus tip excursion (Δz) was measured by opening the feedback loop at $V = 100$ mV (200 mV) in the center of defect- and impurity-free areas ($20 \times 20\ \mathrm{nm}^2$) of Ag (of Cu). The tip was then driven towards the surface at rates ranging from 1 to 2 Å/s recording concomitantly the conductance, and finally retracted by 40 Å. The experimental setup of Ref. [10] was employed to avoid a significant voltage drop at the current preamplifier.

A typical G versus Δz measurement over Ag(111) and Cu(111) is presented in Fig. 1(a). As the tip is approached towards the surface, the conductance increases exponentially up to $G \sim 1$ where a sudden jump to contact is observed. From the exponential tunneling behavior, where $G \propto \exp(-1.025\sqrt{\Phi}\Delta z)$, we extract an apparent barrier height $\Phi = 4.0(2)$ eV and $\Phi = 4.7(2)$ eV for Ag(111) and Cu(111), respectively, typical of metals [4]. A series of jumps acquired with different tips and at different locations of the Ag(111) surface are presented in Fig. 1(b). As shown, the conductance after the jump (G_0), the height of the jump (ΔG), and the tip excursion at which the jump occurs are not completely reproducible.

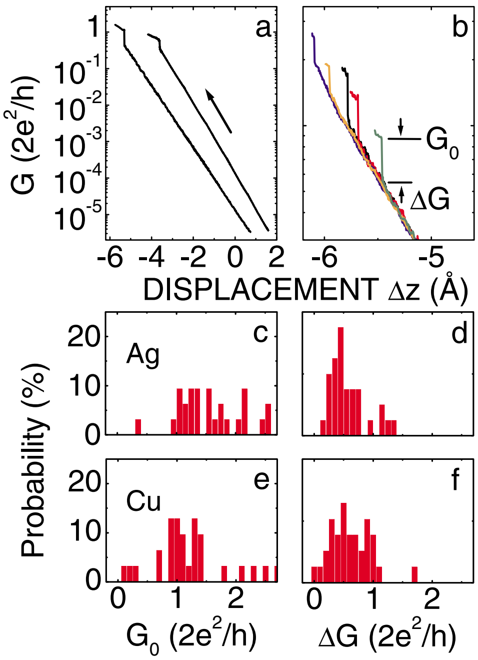

FIG. 1 (color online). (a) Experimental G in units $2e^2/h$ vs Δz for Ag(111) (left) and Cu(111) (right); arrow indicates direction of tip motion. The origin $\Delta z = 0$ is arbitrarily fixed at $G = 1$ nS for Ag(111) and $G = 10$ nS for Cu(111). (b) Degree of reproducibility of the point-contact transition for Ag(111), and histograms of (c) the conductance G_0 after point contact, (d) the conductance-jump ΔG. Histograms of (e) G_0, (f) ΔG for Cu(111).

A survey carried out over 30 jumps observed over Ag(111) [Figs. 1(c) and 1(d)] indicates that $G_0 = 1.5$ and $\Delta G = 0.4$, with large standard deviations of 0.6 and 0.2, respectively. Similarly, a survey over Cu(111) yields $G_0 = 1.1(3)$ and $\Delta G = 0.6(4)$ [Figs. 1(e) and 1(f)].

Figure 2 illustrates an important experimental finding of this Letter. Along with the conductance measurements presented in Fig. 1, we have acquired images prior to [Fig. 2(a)] and after [Fig. 2(b)] the observation of a conductance jump. After a jump, there is a 75% probability for Ag (60% for Cu) that a single atom remains on the surface at the location where the G versus Δz was performed [marked by an arrow in Fig. 2(a)], and a nearly 25% probability (40% for Cu) to find a cluster of atoms [Fig. 2(c)]—in 1 out of 25 approaches no material is transferred to the surface. Figure 2(c) shows that atoms can be transferred in this way from the tip to a desired location of the surface with subnanometric precision. Given our *in situ* tip preparation, the deposited atoms are Ag atoms for Ag(111) and Cu atoms for Cu(111). To confirm this, single atoms were extracted from the Ag and the Cu substrates by indenting the tip 10 Å into the surface. These atoms yielded the same profile in the STM images and the same dI/dV spectrum [11] as the atoms deposited from the tip. This is also an indication that the atom transfer from tip to surface does not damage the substrate in the point-contact region.

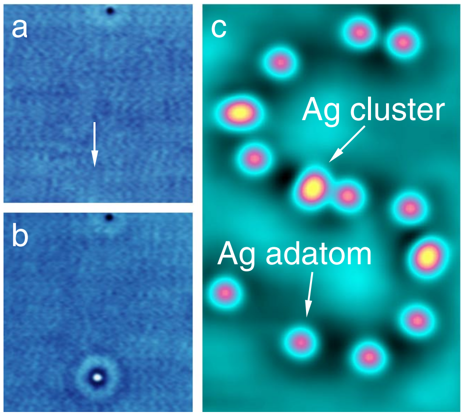

FIG. 2 (color online). Constant current images of the Ag(111) surface (24×24 nm^2, 100 mV, 0.1 nA): (a) prior to, and (b) after the point-contact transition in the conductance (arrow indicates where the tip was approached). (c) Constant current image acquired after a series of point-contact transitions (8×12 nm^2, 100 mV, 0.1 nA).

We extended our study to the conductance of individual Ag and Cu adatoms (Fig. 3). A typical adatom conductance versus displacement curve is shown in Fig. 3(a). The exponential behavior expected for tunneling is observed up to $G \approx 0.1$, but with higher apparent barrier height of $\Phi = 4.6(2)$ eV for Ag and of $\Phi = 5.3(2)$ eV for Cu compared to the clean surfaces. Most importantly, the adatom conductance does not exhibit a sharp jump. Rather, a "glide to contact" is observed: a smooth upturn with respect to the tunneling behavior which sets in at $G \approx 0.3$ and extends over ≈ 0.5 Å, followed by a saturation at a conductance G_0, defined here by the intersection between the experimental curve and the extrapolated tunneling conductance at large tip-sample separations [see Fig. 3(a)]. No material is transferred to the surface. A survey carried out with 20 different tips (on average, 10 approaches were performed for each tip) indicates that $G_0 = 0.93(5)$ for Ag [Fig. 3(b)], and $G_0 = 0.98(6)$ for Cu [Fig. 3(c)], in agreement with break-junctions studies of noble-metal contacts [1]. The number of experimental runs reported is already sufficient to underline that adatom contacts are highly reproducible, contrary to the scatter observed on the clean surfaces.

Before discussing the adatom case, we first focus on the conductance measurements over the clean surfaces. A number of authors have modeled the relaxations effects in a STM when the tip is approached in close proximity of a metallic surface [3,4,12]. It was shown that at interatomic distances of order the typical bond length of the atoms, both tip and surface stretch towards each other because of attractive adhesive forces acting between them. We observe in fact, within experimental error, an exponential variation of G with Δz down to point contact, which, as Olsen *et al.* pointed out [4], is the signature of relaxations effects setting in at least 1 Å before the jump-to-contact occurs. Another experimental signature of relaxation ef-

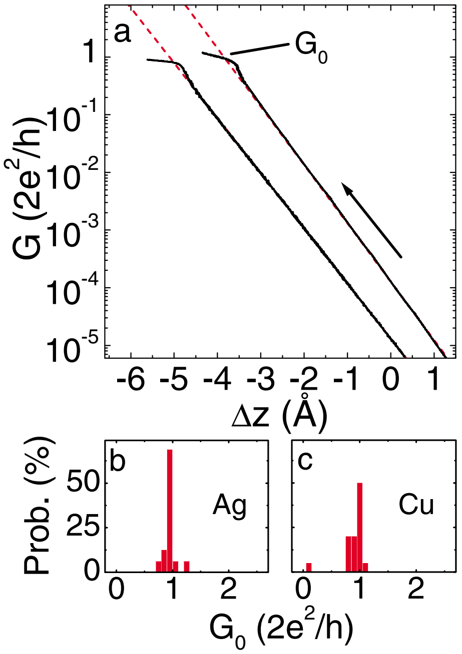

FIG. 3 (color online). (a) Experimental G vs Δz (solid line) and extrapolated tunneling conductance (dashed line) for Ag/Ag(111) (left) and for Cu/Cu(111) (right). The arrow indicates the direction of tip motion ($\Delta z = 0$ at $G = 1$ nS for Ag and at $G = 10$ nS for Cu). (b) Ag/Ag(111) and (c) Cu/Cu(111) histograms of the conductance G_0 after point contact [same binning as in Figs. 1(c) and 1(e)].

fects is the enhanced Stark shift observed in this range for the dI/dV spectra of the Ag(111) surface state [10].

The jump to contact occurs when chemical bonds between the surface and the tip apex start to weaken the adhesion of the atom to the tip structure. In this case, and over a relatively small distance variation of less than 0.1 Å [13], the atom will be transferred from the tip onto the surface. In principle, such an atom transfer could be reversible. However, this was not observed experimentally. To understand the origin of this behavior in detail, we modeled a coupled Cu system by a flat (3 × 3) unit cell and a tip consisting of a Cu pyramid mounted on the reverse of the five layer surface film [12]. At a core-core distance of 3 Å between tip-apex and surface atoms, we performed three separate sets of calculations by standard density functional methods [14]: (i) the apex atom was transferred from the tip onto the surface, while all other atoms were kept frozen. (ii) The tip pyramid and the surface layers were fully relaxed. (iii) The tip pyramid was kept frozen; only surface atoms were relaxed. In the first case we observe a parabolic energy distribution, with a minimum for the apex atom centered between the surface and the tip. In the second case we observe strong outward relaxation of the surface layer, coupled to the transfer of the apex atom onto the surface. The total energy gain by relaxations amounts to about 1 eV/atom in the interface. Our numerical methods in the third case indicate that surface atoms are removed from the surface to form a cluster with the tip apex, in contrast to the experimental findings. This confirms that the atom transfer can only occur from the tip to the surface, the reverse transfer necessitating an unrealistic nonrelaxed tip. We conclude from these results that the tip-apex atom will be transferred in every case once the distance is well below the jump-to-contact point. Under ambient thermal conditions transferred tip atoms may diffuse rapidly to the step edges of the crystal and therefore not be observed. The analysis also confirms that a one-atom contact is formed during the approach, which is otherwise inferred from the value of G close to the quantum of conductance.

The random character of the jump to contact over the clean surfaces (Fig. 1) can be understood in the light of recent simulations [12]. It was shown that the jump to contact strongly depends on where the approach is performed on the surface. Regardless of its chemical nature, when the tip is positioned on top of a surface atom, the jump should be detected about 0.5 Å earlier compared to a threefold hollow position, all other locations on the surface exhibiting a jump within this range. Following this viewpoint, since surface atoms are not usually resolved—this is quite common for compact (111) surfaces—the conductance measurements are performed at random locations of the surface, and the jumps occur randomly within a finite excursion range of the tip. Based on the data, this range is estimated to be 0.5 Å for Ag [Fig. 1(b)] and 0.3 Å for Cu, in good agreement with the above prediction. The random nature of G_0 and ΔG indicate that conformation changes of the interface may affect electronic transport properties quite substantially, as recent transport simulations on Al(111) pointed out [15]. Over the adatoms, however, where the two systems approach contact on a well defined location, the conductance is reproducible [Figs. 3(b) and 3(c)].

The atomic arrangement and the conductance properties of single adatoms Cu/Cu(111) and Ag/Ag(111) were simulated by two sets of calculations: (i) In a density functional simulation of a five layer surface film with an atomically sharp tip model we calculated the relaxed positions of surface and tip at intervals of 0.2 Å. (ii) The conductance properties were also calculated during the approach, taking into account the shift of atomic positions with a recently developed model [13]. As the first set of simulations reveals, the atomic positions are only slightly relaxed during the transition from the tunneling regime to point contact [Fig. 4(a)]. This is in sharp contrast to the situation on a flat surface, where the tip will be fractured, as shown above by experiments and simulations [see also Fig. 4(b)]. The reason for this marked difference is the larger stiffness of the adatom bond to the surface. We find an increase of the elastic constants on Cu (Ag) to 6.1(5.1) eV/Å^2, which is nearly double the value found on flat surfaces [13]. This indicates that the redistribution of surface charge due to the Smoluchowski effect creates a surface dipole which enhances the bonding of the adatom.

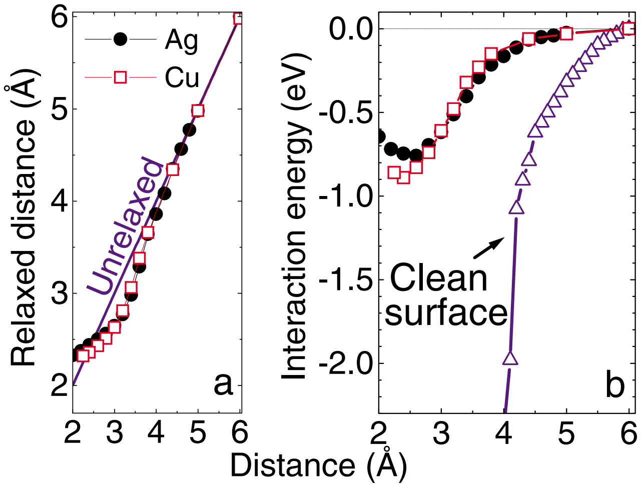

FIG. 4 (color online). Calculated results for adatoms. (a) Actual tip-adatom distance (relaxed distance) vs distance in the absence of tip-sample interaction. Intersection with the unrelaxed curve (solid line) indicates transition from attractive to repulsive regime. (b) Adatom interaction with the tip vs distance. The onset of strong chemical attractions occurs at about 4 Å. Open triangles: calculated tip interaction with the clean Au(111) surface [12,13]. Tip fracture occurs at 4.2 Å.

Without a dipolar interaction, surface atoms and adatoms would have roughly the same elastic constant, since the elastic properties are governed by the p-orbital bonds with their three underlying atoms. Moreover, in both cases the tip-adatom interaction, contrary to the tip-surface one, remains well below 1 eV [Fig. 4(b)], which was identified as the threshold value for jump to contact and atom transfer. Based on these findings, it can be concluded that the reproducible transition from the tunneling to the contact regime is due to the comparatively small and reversible relaxations.

The conductance was simulated with Bardeen's method. The only effect of interactions included in the simulation was the relaxation of the adatom. However, in this situation the strong localization of the adatom wave functions, in combination with an atomically sharp tip, will lead to large changes of the crystal potential in the immediate vicinity of the point contact even for larger distances [16]. Since the exponential decay of the wave functions reflects these potential changes, perturbation methods become unreliable. The exponential decay constants were therefore calculated for large distances of 9 Å, where the two systems will be completely decoupled. Here, at the position of the adatom (on the flat surface) the apparent barrier height is $\Phi = 5.0(4.4)$ eV for Cu and $\Phi = 4.6(4.0)$ eV for Ag. The simulated values agree very well with experimental findings. Interestingly, a drop of the potential barrier by about 1 eV at a distance of 6 Å is also observed in the simulations. That the barrier height remains close to constant in this range cannot be due to atomic relaxations. It seems, therefore, that the localization of electron states on single atoms at both sides of the tunneling junction leads to a substantial change of the potential barrier even in this range. We shall analyze this feature in future simulations.

Summarizing, a sharp jump in the conductance is observed when a metallic tip is brought into contact with a compact (111) metallic surface. The jump is associated with an irreversible tip fracture, which, in most cases, results in the transfer of the tip-apex atom to the surface. This is experimental evidence that a one-atom contact is formed. When contacting single adatoms, on the contrary, no material is transferred, and a smooth and reproducible transition occurs from tunneling to contact regime. Single-adatom contacts with a STM are therefore junctions which can potentially be employed to probe electron transport through single atoms, and eventually molecules, with knowledge of number and identity of the atoms in between electrodes.

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Note added.—Recently, we became aware of related work for Mn and Gd atoms on Cu(100) [17].

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